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SPECIFICATION

INTERNAL MEMBER FOR PLASMA-TREATING VESSEL AND METHOD OF PRODUCING THE SAME

TECHNICAL FIELD

This invention relates to an internal member for plasma-treating vessel having an excellent resistance to plasma erosion and a method of producing the same.

Particularly, the invention is a technique capable of applying to members used in a plasma treatment under a plasma environment using a treating gas containing a halogen element such as deposit shield, baffle plate, focus ring, insulator ring, shield ring, bellows cover, electrode and so on.

Moreover, the invention is applicable to internal parts for plasma-treating vessels in a field of a semiconductor manufacturing device, a manufacturing apparatus for a liquid crystal device or the like.

BACKGROUND ART

In general, a fluoride such as BF_3 or NF_3, a chloride such as BCl_3 or $SnCl_4$, a bromide such as HBr, or the like is used as a treating gas for various treatments in the manufacturing process of semiconductors, liquid crystal devices and the like, so that there is a problem that parts in the treating vessel are considerably corroded and damaged.

For instance, as a material used in the plasma-treating vessel for the semiconductor manufacturing apparatus, there are known a metallic material such as Al, Al alloy or the like, an anodized oxide film of Al covering the surface of the metallic material, a sprayed coating such as boron carbide or the like, a sintered body film of Al_2O_3, Si_3N_4 or th like, and a high polymer film of fluorin r sin, poxy r sin or the like. Th se mat rials

are known to b subjected to a chemical damage when b ing contacted with a halog n ion indicating a strong corrosive property, or to an erosion damage through fines particles of SiO_2 and Si_3N_4 and an ion excited by a plasma.

Especially, a plasma is frequently used for more activating the reaction in the process using a halogen compound. However, the halogen compound is dissociated to atomic F, Cl, Br, I or the like indicating a very strong corrosive property under an environment using such a plasma. Even in this case, if a finely divided solid of SiO_2, Si_3N_4, Si, W or the like is existent in such an environment, the member used in the plasma-treating vessel is strongly subjected to not only the chemical corrosion but also the erosion damage through the above fine particles.

And also, the environment excited by the plasma is ionized even by a gas having no corrosive property such as Ar gas to cause a phenomenon of strongly impinging to a solid face (ion bombardment), so that various members arranged in the above vessel are subjected to a stronger damage.

Heretofore, there was a method of forming a thin Al_2O_3 film or the like as a technique adopted when being subjected to such a chemical corrosion or erosion damage. However, such a technique has the following problems.

(1) With respect to a material covered with Al_2O_3 film (alumite) by subjecting Al and Al alloy to an anodization to provide corrosion resistance, there is a problem that the service life becomes shorter when being subjected to plasma erosion in an environment containing a halogen gas. And also, since it is an Al-containing film, AlF_3 particles are created, which bring about a fear of degrading quality of semiconductor product manufactured.

(2) There is a technique that a dense film of oxide, carbide, nitride, fluoride or the like of Group 3a el m nt in the Periodic Table such as Sc, Y, La, C , Yb, Eu, Dy or th like is formed on the surfac of a part through

PVD or CVD proc ss, or a singl crystal of Y_2O_3 is applied ther to (JP-A-10-4083). However, this t chniqu has problems that the film forming rate is slow and the productivity is poor and plural film members (composite film) can not simultaneously be formed.

It is, therefore, an object of the invention to propose a surface-treated member for plasma-treating vessel or the like having large resistances to damage due to chemical corrosion and damage through plasma erosion under environment containing a halogen gas as well as a method of producing the same.

DISCLOSURE OF THE INVENTION

The invention solves the aforementioned problems and drawbacks of the conventional techniques by adopting means as mentioned below. That is, the construction of the invention is as follows:

(1) A cover member comprising a substrate and a layer of Y_2O_3 sprayed coating having a porosity of 0.2-10% and a thickness of 50-2000 μm formed on a surface of the substrate through a thermal spraying process.

(2) A cover member comprising a substrate, and a composite layer consisting of a coating of one or more metals or alloys selected from Ni and an alloy thereof, W and an alloy thereof, Mo and an alloy thereof and Ti and an alloy thereof, which are excellent in an adhesion property to Y_2O_3 sprayed coating, formed at a thickness of 50-500 μm as an undercoat on a surface of the substrate under a plasma generating condition in an environment containing a halogen compound through, preferably, a thermal spraying process and a Y_2O_3 sprayed coating formed at a thickness of 50-2000 μm on the undercoat in case of an environment having a strong corrosion property.

(3) A cover member comprising a substrate and a multilayer composit layer consisting of th above metal coating (pr f rably spray d coating) form d on a surfac of

th substrat as an und rcoat, a Al_2O_3 coating (pref rably spray d coating) form d on the undercoat as a middle lay r and the above Y_2O_3 sprayed coating formed on the middle layer as a topcoat through thermal spraying in case of an environment having a strong corrosion property.

(4) A cover member comprising a substrate and a multilayer composite layer consisting of the above metal coating (preferably sprayed coating) formed on a surface of the substrate as an undercoat, a film of Al_2O_3 and Y_2O_3 (preferably sprayed coating) formed on the undercoat as a middle layer and the above Y_2O_3 sprayed coating formed on the middle layer as a topcoat through thermal spraying in case of an environment having a strong corrosion property.

(5) A cover member is covered with the Y_2O_3 sprayed coating directly formed on the surface of the substrate or indirectly formed through the undercoat or middle layer in the above method, wherein the sprayed coating is obtained by using Y_2O_3 powder having a purity of not less than 95% and adopting a spraying method selected from plasma-spraying the powder in air, plasma-spraying in an Ar gas containing no oxygen under a reduced pressure, high-speed flame spraying, explosion spraying and the like.

Among them, the method of plasma-spraying under the reduced pressure of Ar gas is also effective for the improvement of the corrosion resistance.

BEST MODE FOR CARRYING OUT THE INVENTION

The inventors have made studies in order to solve the aforementioned problems of the conventional techniques and confirmed that the damage of the internal member for the plasma-treating vessel is a damage due to chemical corrosion through a halogen gas and a damage due to plasma erosion. And also, it has been found that when the member is used in an environment containing the halogen excited by the plasma, it is important to pr v nt th damag caus d by the r sistanc to the plasma erosion, which is th n

eff ctive to prev nt th ch mical corrosion.

To this end, the inv ntors have made mainly the formation of the coating effective for the resistance to plasma erosion. As a result, the above member according to the invention is developed.

That is, the invention adopted as means for solving the above subject is fundamentally a member obtained by forming a sprayed coating consisting of only Y_2O_3 on a surface of a substrate such as metal, ceramic, carbon material or the like through thermal spraying process. In case of a strong corrosive environment using the above member, there is developed a member obtained by forming an undercoat of a metal having a strong resistance to halogen gas corrosion beneath the above Y_2O_3 sprayed coating and further forming a middle layer of Al_2O_3 or Y_2O_3.

The construction of the member according to the invention is described in detail below.

(1) Substrate

As a substrate for forming the sprayed coating, various steels inclusive of stainless steel, aluminum and aluminum alloy, tungsten and tungsten alloy, titanium and titanium alloy, molybdenum and molybdenum alloy, carbon and oxide or non-oxide ceramic sintered body, a carbonaceous material and the like are favorable.

Moreover, copper and copper alloy are unfavorable because they are subjected to plasma erosion or corrosion through a halogen compound to bring about environmental contamination. Therefore, if the use of copper or copper alloy is required in view of apparatus construction, they are required to be covered with Cr, Ni or the like by electrolytic plating, chemical plating, vapor deposition or the like.

(2) Construction of sprayed coating

The sprayed coating is preferable to be formed on th surfac of th substrat by subjecting the substrat to a shot blast treatment and th n dir ctly thermal spraying

Y_2O_3, or by forming a film or sprayed coating of a m tal material having a strong resistanc to corrosion through a halogen gas as an undercoat layer on the surface of the substrate by PVD treatment, CVD treatment or thermal spraying treatment and then spraying Y_2O_3 powder on the undercoat as a top coat. In the latter case, the film thickness of the metal undercoat (sprayed coating or the like) is within a range of 50-500 μm. When the undercoat layer is thinner than 50 μm, the action and effect as the undercoat become weak, while when it exceeds 500 μm, the effect is saturated and there is no meaning on the thickening.

As the metal material for the undercoat, nickel and nickel alloy, tungsten and tungsten alloy, molybdenum and molybdenum alloy, titanium and titanium alloy and so on are preferable.

On the other hand, the Y_2O_3 sprayed coating as a top coat is favorable to have a thickness of 50-2000 μm even when it is directly formed on the surface of the substrate or when it is sprayed onto the undercoat to form a composite layer or further when Al_2O_3 or Al_2O_3+Y_2O_3 coated film is formed as a middle layer. Because, when the thickness is less than 50 μm, the effect on the prevention of the damage due to the plasma erosion is poor, while when it exceeds 2000 μm, the effect is saturated and there is no meaning in the economical reason.

Moreover, the porosity of the Y_2O_3 sprayed coating as a top coat is preferably within a range of 0.5-10%. It is difficult to produce the sprayed coating having the porosity of less than 0.5% by the spraying method, while the coating having the porosity of more than 10% is poor in the corrosion resistance and the resistance plasma erosion.

(3) Y_2O_3 sprayed coating as an outermost layer on member

A most characteristic construction of the inv ntion li s in that Y_2O_3 is adopt d as a material indicating the resistanc to plasma rosion in an

environment containing a halogen gas and form d as a sprayed coating lay r as a structur of an out rmost surface layer of the substrate. As a result of the inventors' studies, it has been found that since Y_2O_3 has a specific gravity of 4.84 and a melting point of 2410°C and is strong in the chemical bonding force to oxygen, it maintains a stable state even if the action of plasma erosion is suffered in the atmosphere containing the halogen gas. In this case, however, it is required to use Y_2O_3 having a purity of not less than 95%. If an impurity such as Fe, Mg, Cr, Al, Ni, Si or the like is contained as an oxide, the erosion resistance is unfavorably lowered. The purity is more favorable to be not less than 98%.

Moreover, Al_2O_3 as a middle layer formed just beneath the Y_2O_3 sprayed coating is chemically stable and less in the change under environment of plasma spraying at atmospheric pressure or plasma spraying under a reduced pressure and serves to compensate the resistance to plasma erosion of Y_2O_3.

(4) Coating method

a. Formation of sprayed coating

In the invention, Y_2O_3 coating as a top coat in at least outermost layer is a sprayed coating. Further, it is preferable that the whole structure of the coating is rendered into the following multilayer structure in order to strengthen the sprayed coating of the top coat.

That is, an undercoat of a metal sprayed coating is formed on the surface of the substrate and Al_2O_3 sprayed coating or a mixture sprayed coating of Al_2O_3 and Y_2O_3 in the gradient compounding is formed thereon as a middle layer and further Y_2O_3 sprayed coating is formed thereon as a top coat.

The reason why the above coating structure is preferable is due to the fact that by forming as the middle layer Al_2O_3 having exc ll nt corrosion resistance and r sistance to plasma erosion as compar d with th m tal

spray d coating is rendered the sprayed coating into a multilayer structur , and th through-hol s of the coating is decreased to improve the corrosion resistance and the resistance to erosion. Furthermore, Al_2O_3 as the middle layer develops good adhesion property to both of the undercoat and the top coat. In this meaning, the middle layer is favorable to be a mixture layer of Al_2O_3 and Y_2O_3. In this case, the mixture layer is favorable to be based on the gradient compounding that the Al_2O_3 concentration at the undercoat side becomes high and the Y_2O_3 concentration at the top coat side becomes high. The formation of such a middle layer can easily be carried out by adopting a spraying process, so that it is said to be a preferable embodiment that the middle layer is formed as a sprayed coating. Moreover, the thickness of the middle layer is favorable to be within the same range as the Y_2O_3 sprayed coating of the top coat.

In the invention, a plasma spraying process under an atmospheric pressure or a plasma spraying process in an atmosphere containing substantially no oxygen is favorable for forming a sprayed coating of metal or Al_2O_3 or Y_2O_3, but it is also possible to conduct a high-speed flame spraying process or an explosion spraying process.

b. Formation of undercoat, middle layer through CVD process or PVD process

In the CVD process, steam of a halogen compound of a desired metal is reduced by hydrogen or the like and then oxidized by oxygen or an oxygen compound, and changed into an oxide film by heating in air.

In the PVD process, a sintered body or powder is used as a starting material and evaporated by irradiating an electron beam to precipitate onto the surface of the substrate to form a film.

In general, the formation of the film through CVD proc ss or PVD process is suitabl for forming thin film (.g. about 50 μm).

(5) Environment using th member according to the invention

The Y_2O_3 sprayed coating covered onto the surface of the member according to the invention is particularly useful for the use under plasma environment generated in an atmosphere containing a halogen compound.

Of course, the invention is effective even to a plasma erosion action in an environment containing no halogen element or halogen compound such as N_2, H_2 or the like. In this case, erosion damage becomes gentle as compared with the environment containing the halogen element or compound, so that the sprayed coating member according to the invention develops a stable performance over a long time.

EXAMPLE

Example 1

In this example, a one-side surface of an aluminum test piece (size: width 50 mm x length 50 mm x thickness 5 mm) is roughened by a shot blast treatment and Y_2O_3 sprayed coating having a thickness of 300 μm is formed by using Y_2O_3 spraying material through a plasma spraying process under an atmospheric pressure or a plasma spraying process under a reduced pressure controlled to an atmosphere pressure of 50-200 hPa with Ar gas, respectively.

And also, an undercoat of Ni-20% Al alloy is formed on a one-side surface of an aluminum test piece at a thickness of 100 μm by a plasma spraying process under an atmospheric pressure and the above Y_2O_3 is formed thereon at a thickness of 300 μm as a top coat.

Thereafter, the porosity and adhesion strength of the Y_2O_3 sprayed coating formed on the surfaces of these test pieces are measured and thermal shock test (test of repeating a cycle of an operation that the piece is heated in an electric furnace held at 500°C for 20 minutes and cool d in air at the outside of th furnac 10 tim s) is conduct d. Mor ov r, Al_2O_3 spray d coatings form d und r

the sam conditions at th sam steps as m ntioned above ar us d as a comparative example.

The test results are shown in Table 1.

All of the coatings according to the invention, i.e. Y_2O_3 sprayed coatings directly coated on the surface of the test piece (Nos. 1, 3) and Y_2O_3 sprayed coatings formed on the undercoat (Nos. 2, 4) show good adhesion property and resistance to thermal shock, which are in no way inferior to those of the Al_2O_3 film. Particularly, the Y_2O_3 coating formed by the plasma spraying process under a reduced pressure is smaller in the porosity as compared with that of the coating formed by the spraying process under an atmospheric pressure and can expect the good corrosion resistance.

(Table 1)

No.	Spraying Process	Structure of coating		Porosity (%)	Adhesion strength (MPa)	Visual appearance in thermal shock test	Remarks
		Under coat	Top coat				
1	Atmospheric plasma spray	None	Y_2O_3	5 ~ 9	35 ~ 38	No peeling	Example
2		Ni-20Al	Y_2O_3	6 ~ 8	38 ~ 41	No peeling	
3	Low pressure plasma spray	None	Y_2O_3	0.2 ~ 3	40 ~ 41	No peeling	
4		Ni-20Al	Y_2O_3	0.3 ~ 4	40 ~ 44	No peeling	
5	Atmospheric plasma spray	None	Al_2O_3	8 ~ 12	38 ~ 42	No peeling	Comparative Example
6		Ni-20Al	Al_2O_3	9 ~ 12	35 ~ 44	No peeling	
7	Low pressure plasma spray	None	Al_2O_3	0.5 ~ 5	38 ~ 44	No peeling	
8		Ni-20Al	Al_2O_3	0.6 ~ 7	39 ~ 43	No peeling	

(Note)

(1) Coating thickness: undercoat 100 μm, top coat 300 μm

(2) Adhesion strength is according to a test method of adhesion strength defined in test method of ceramic coating in JIS H8666

(3) Th rmal shock test: 500°C x 20 min → room t mperatur

(air cooling) observation of app arance after repetition 10 tim s.

Example 2

In this example, an aluminum substrate of 50 mm x 100 mm x 5 mm thickness is used and subjected to a surface treatment as shown in Table 2 and a test piece having a size of 20 mm x 20 mm x 5 mm is cut out from the substrate and a portion is masked so as to expose the surface treated face in a range of 10 mm x 10 mm and irradiated for 20 hours under the following conditions and measured is a damage quantity through plasma erosion as a reduced thickness.

(1) Environmental gas and flow rate condition

A mixed gas of CF_4, Ar and O_2 is an atmosphere under the condition.

$CF_4/Ar/O_2$ = 100/1000/10 (flow rate cm3 per 1 minute)

(2) Plasma irradiation output

High frequency power: 1300 W

Pressure: 133.3 Pa

The test results are shown in Table 2. As seen from the results of Table 2, the anodized film (No. 8) of a comparative example (existing technique) and B_4C sprayed coating (No. 10) are large in the damage quantity through the plasma erosion and are not put into practical use. Moreover, the Al_2O_3 coating (No.9) shows a relatively good resistance to plasma erosion among the comparative examples.

On the contrary, the Y_2O_3 sprayed coatings according to the invention develop a very excellent resistance to plasma erosion and maintain good performances even in an environment containing a halogen compound.

(Table 2)

No.	Sprayed materials	Surface treatment	Presence or absence of undercoat	Damag d depth through erosion (μm)	Remarks
1	Y_2O_3 (99.9%)	Spraying	Presence	6.2	Example
2			Absence	6.1	
3	Y_2O_3 (99.8%)	Spraying	Presence	7.6	
4			Absence	7.2	
5	Y_2O_3 (99.5%)	Spraying	Presence	6.5	
6			Absence	6.3	
7	Y_2O_3 (99.9%)	PVD	Absence	6.6	Compara-tive example
8	Al_2O_3	Anodizing	Absence	39.5	
9	Al_2O_3	Spraying	Presence	8.1	
10	B_4C	Spraying	Presence	28.0	
11	Quartz	-	Absence	39.0	

(Note)

(1) The spraying is carried out by a plasma spraying process under an atmospheric pressure and the thickness of undercoat is 80 μm and the thickness of top coat such as Y_2O_3, Al_2O_3 or the like is 200 μm.

(2) Material of undercoat is 80% Ni-20% Al.

(3) Anodizing is carried out according to AA25 defined in JIS H8601.

Example 3

In this example, 80% Ni-20% Al of 80 μm in thickness as an undercoat, Al_2O_3 or a mixture of Al_2O_3 50 vol%/Y_2O_3 50 vol% of 100 μm as a middle layer and Y_2O_3 of 200 μm in thickness are formed on an aluminum substrate of width 50 mm x length 100 mm x thickness 5 mm by a plasma spraying process under an atmospheric pressure, resp ctiv ly, and th n a plasma erosion test is carried out under th same conditions as in Exampl 2.

As a r sult, since th Y_2O_3 sprayed coating is

formed on the out rmost surface layer portion (top coat), ven when Al_2O_3 or th mixtur lay r of Al_2O_3/Y_2O_3 is form d as the middle layer, the resistance to plasma erosion is not influenced in the sprayed coating according to the invention and only a loss of 6.1-7.5 μm is observed by irradiation for 20 hours, and hence it is recognized to develop sufficient performances even in the multilayer structure coating.

Example 4

In this example, with respect to a test piece obtained by anodizing the existing aluminum substrate (alumite treatment) and a test piece formed by covering a 80% Ni-20% Al alloy coating of 100 μm in thickness on the substrate as an undercoat and coating a Y_2O_3 coating of 250 μm in thickness thereon as a top coat through plasma spraying process is carried out a plasma etching under the following conditions to measure the number of particles flied through the etching as particle numbers adhered onto a surface of a silicon wafer of 8 inches in diameter placed on the same chamber. Moreover, the number of particles adhered is examined by a surface inspection apparatus based on particles having a particle size of not less than approximately 0.2 μm.

(1) Environmental gas and flow rate condition

A mixed gas of CHF_3, O_2 and Ar is an atmosphere under the condition.

$CHF_3/O_2/Ar$ = 80/100/160 (flow rate cm3 per 1 minute)

(2) Plasma irradiation output

High frequency power: 1300 W

Pressure: 4 Pa

Temperature: 60°C

As a result of this experiment, in the anodized test piece (alumite film), the particle number exceeds 30 particles as a particle control value in the general chamb r aft r 17.5 hours of th plasma irradiation and is not l ss than 150 particles aft r 25 hours. Th

composition of the particle consists of Al and F.

On th contrary, in the Y_2O_3 sprayed coating according to the invention, the particle number only exceeds the control limit value even after 70 hours of the irradiation and the excellent resistance to plasma erosion is indicated.

INDUSTRIAL APPLICABILITY

As mentioned above, according to the invention, the member obtained by directly forming Y_2O_3 sprayed coating on the metallic or non-metallic substrate or by forming a metallic undercoat and then forming Y_2O_3 sprayed coating shows an excellent resistance when it is used under an environment subjected to plasma erosion action in a gas atmosphere containing a halogen compound. To this end, even when plasma etching operation is continued over a long time, the contamination through particles in the chamber is less and it is possible to efficiently produce a high quality product. And also, the contamination rate of the particle in the chamber becomes slower, so that the interval for the cleaning operation becomes long and the improvement of the productivity can be expected. As a result, the members according to the invention are very effective as an internal member for a plasma treating vessel in the field of semiconductor production apparatus, liquid crystal device or the like.